

Tables 3-2 and 3-3 summarize U.S. registration and classification histories of aldrin and dieldrin, respectively.

Table 3-2. Aldrin Registration and Classification History (CAS # 309-00-2)

Action	Federal Register Notice	Action Date
Registration canceled for the following uses: almonds, avocados, beans (except seed treatment), blackberries, blueberries, boysenberries, buckwheat, cashews, chestnuts, cotton (except seed treatment), currants, dates, dewberries, figs, filberts, flax, gooseberries, guavas, hazelnuts, hickory nuts, hops, huckleberries, kumquats, loganberries, mint, okra, olives, papayas, passion fruit, peanuts (seed), pecans, persimmons, pomegranate, raspberries, safflower (except seed treatment), sorghum (except seed treatment), sugarcane (bait use only), tangelos, walnuts, youngberries, and greenhouse use.	34 FR 7712	5/69
Registration canceled for bananas and safflower.	35 FR 7136	4/70
All uses and production suspended except subterranean termite control and for dipping of roots and tops of non-food plants and moth-proofing in manufacturing processes using totally enclosed systems. Continued sale and use of existing stocks formulated prior to August 2, 1974 permitted.	3 9 F R 37246	1974
Tolerances of Aldrin revoked.	5 1 F R 46662	12/86

Table 3-3. Dieldrin Registration and Classification History (CAS # 60-57-1)

Action	Federal Register Notice	Action Date
Registration canceled for cotton (foliar and soil applications).	35 FR 7136	4/70
All uses and production suspended except subterranean termite control and for dipping of roots and tops of non-food plants and moth-proofing in manufacturing processes using totally enclosed systems. Continued sale and use of existing stocks formulated prior to August 2, 1974 permitted.	3 9 F R 37246	1974
Tolerances of dieldrin revoked.	5 1 F R 46662	12/86

3.1.2 Manufacture and Distribution of Aldrin and Dieldrin

Aldrin was first synthesized in the United States as a pesticide in 1948. Manufacture in the United States was by only one firm, Shell Chemical Company, and it has not been produced in the United States since 1974 (USDHHS, 1993).

Dieldrin was manufactured by the epoxidation of aldrin. Dieldrin was also solely manufactured in the United States by Shell Chemical Company. Manufacture of dieldrin in the United States was also stopped in 1974 (USDHHS, 1993).

The 1997/98 Directory of World Chemical Producers, reports that limited amounts of aldrin are still being produced in India. No other production information on dieldrin or aldrin was found during this study, nor was any other information located on current or historical manufacturers or uses in other countries.

3.1.3 Aldrin and Dieldrin Uses

Aldrin and dieldrin are active against insects by contact or ingestion. The primary use of these products was for control of corn pests by application to the soil (USDHHS, 1993). Other past uses were in the citrus industry and in general crop protection. Non-agricultural pesticide use included application against termite infestation of structures and against soil-dwelling pests such as ants, wireworms, and whitegrubs.

Aldrin use in the United States peaked at 19 million pounds in 1966. By 1970 use had decreased to 10.5 million pounds. From 1966-1970, the amount of dieldrin used in the United States declined from 1 million pounds annually to approximately 670,000 pounds. This decrease was attributed to increased insect resistance to the two chemicals and to the development and availability of more effective and environmentally safer pesticides (USDHHS, 1993; USNLM 1998a,b). All U.S. manufacture and use of aldrin and dieldrin has been discontinued (USNLM, 1998a). Figure 3-1 shows the use in pounds of both aldrin and dieldrin by state in 1971 (Majewski and Capel, 1995) as well as the concentrations found in air measured in 1976 and the detection frequency relative to the number of sites sampled for air measurements. Aldrin application appeared highest in many of the states adjacent to the southern edge of the Great Lakes. Conversely, dieldrin use appeared relatively low in the Great Lakes region. The detection frequency of dieldrin was twice as high as for aldrin, which is not surprising, given the fact that aldrin converts readily to dieldrin in the environment.

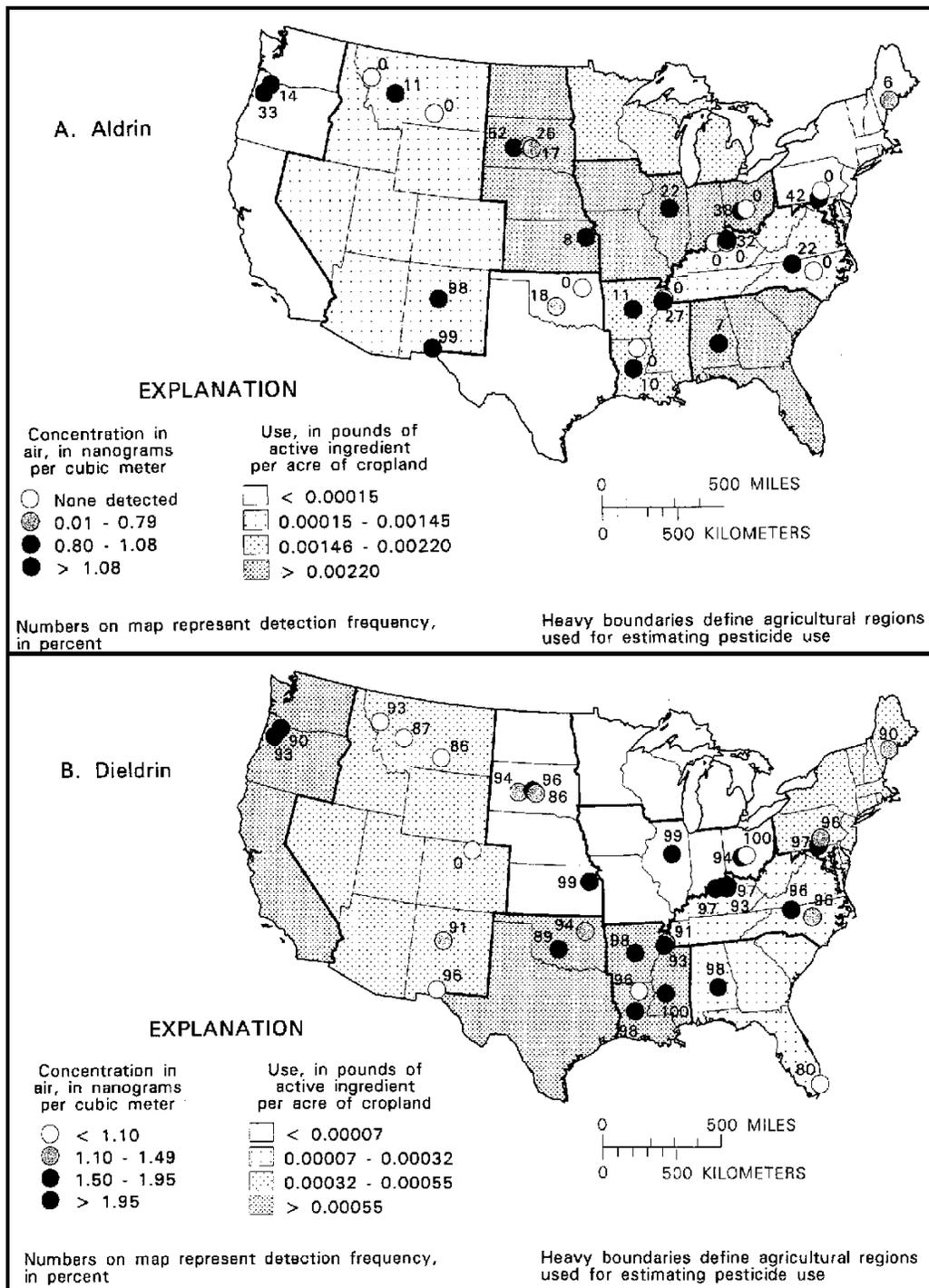


Figure 3-1. Average range of measured concentrations of (A) aldrin and (B) dieldrin in air and the detection frequency. (NOTE: Concentrations measured from 1960-1970; agricultural use in 1970.)

Source: *Pesticides in the Atmosphere, Distribution, Trials & Governing Factors* (Majewski & Capel, 1995)

3.1.4 Description of Product Components/Structure, Manufacturing Byproducts/Degradation

Aldrin (CAS #309-00-2) in its pure form is a white crystalline solid. The physical properties of aldrin are given in Table 3-4. Figure 3-2 presents the molecular structure of aldrin. Technical grade was reported with the following composition: 90.5% hexachlorohexahydrodimethanonaphthalene (HHDN), 3.5% isodrin; 0.6% HCB, 0.5% chlordane, 0.5% octachlorocyclopentane, 0.3% toluene and ~4% other compounds (USDHHS, 1993).

Table 3-4. Physical Properties of Aldrin

Properties	Value
Melting Point	104° C - pure; 49-60° C-technical
Boiling Point	145° C @ 2mm Hg
Henry's Law Constant (KH)	4.96x10 ⁻⁴ atm m ³ /mol @25° C
Log K _{oc}	2.61-4.69
Log K _{ow}	3.01 - 7.4
Water Solubility	17-180 ug/L @ 25° C
Vapor Pressure	2.31x10 ⁻⁵ mm Hg @ 20° C

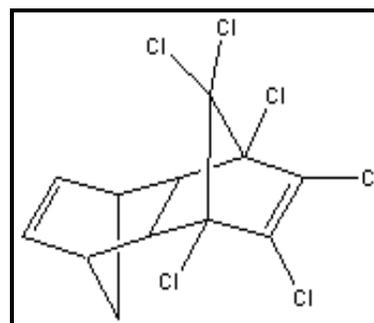


Figure 3-2. Aldrin Molecular Structure

Source: Ritter *et al.*, Assessment Report, Dec 1995 (PCS 95.39); USDHHS, 1993)

The chemical synthesis of dieldrin (CAS #60-57-1) is by epoxidation of aldrin. The physical properties of dieldrin are given in Table 3-5. Dieldrin in its pure form is a white crystalline solid and technical grade is a tan color. The molecular structure of dieldrin is presented in Figure 3-3. In the environment, aldrin is readily converted to dieldrin through biodegradation.

Table 3-5. Physical Properties of Dieldrin

Properties	Value
Melting Point	175-176° C
Boiling Point	decomposes
Henry's Law Constant (KH)	5.8×10^{-5} atm m ³ /mol @25° C
Log K _{oc}	4.08-4.55
Log K _{ow}	3.69-6.2
Water Solubility	140 ug/L at 20° C
Vapor Pressure	1.78×10^{-7} mm Hg @ 20° C

Source: Ritter *et al.*, Assessment Report, Dec 1995 (PCS 95.39)

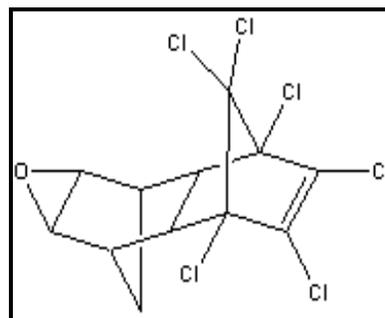


Figure 3-3. Dieldrin Molecular Structure

3.1.5 Product Export and Import

Prior to the 1974 cancellation for all food crops and most other agricultural uses, neither aldrin nor dieldrin were imported into the United States. From 1974-1985, aldrin was imported from Shell International (Netherlands) for formulation and limited use. Between 1981 and 1985, an estimated 1-1.5 million pounds of aldrin were imported annually to the United States. EPA reports that aldrin has not been imported since 1985. No information was found detailing dieldrin importation (USDHHS, 1993)

No information was found on U.S. export amounts of either aldrin or dieldrin. Companies were not required to track or report export amounts. Therefore, confirming historical quantities shipped abroad is difficult.

3.2 Mirex

Mirex, also known as Dechlorane, was used as both a pesticide and a fire retardant.

3.2.1 Registration and Classification Status of Mirex

Production of most registered pesticide products containing mirex was canceled on December 1, 1977. However, selected ground application was allowed until June 30, 1978, at which time the uses of the product were canceled in the United States; the exception being continued use in Hawaii on pineapples until stocks were exhausted. The registration history of mirex is summarized in Table 3-6.

Other Currently Non-Regulated Uses for Mirex

Mirex, or dechlorane, may have been used as a color enhancing agent in fireworks. It is still currently available for purchase for this use.

Table 3-6. Mirex Registration and Classification History (CAS # 2385-85-5)

Action	Federal Register Notice	Action Date
<p>Registration for Mirex 4x Bait was canceled December 1, 1976. Between July 1, 1976 and December 1, 1976 not more than 45,000 pounds of technical mirex was to be formulated into Mirex 4x Bait. Stocks of 4x Bait existing after December 1, 1976 to be used only through December 31, 1976, provided that 1,000 pounds were used for research until June 30, 1978.</p>	41 FR 56703	1976
<p>Registration for Mirex 10:5 Bait canceled December 1, 1977. Existing stocks in five pound bags could be sold, distributed and used in ground broadcast and mound application until June 30, 1978. Other existing stocks were packaged into five pound bags and sold, distributed and used in ground broadcast and mound application.</p>	41 FR 56703	1977
<p>Technical mirex was canceled December 1, 1977. Existing stocks were not to be distributed, sold, or used after December 1, 1977.</p>	41 FR 56703	1977
<p>Registration for Mirex Harvester Ant Bait 300 canceled December 29, 1976 for all uses other than for the control of the phaidole ant, the Argentine ant, and the fire ant on pineapples in Hawaii. Existing stocks distributed, sold and used for all uses until December 31, 1976. Cancellation for control of said ant on pineapples in Hawaii December 1, 1977. Stocks existing on December 1, 1977 were not to be applied aerially for control of said ants, but could be distributed, sold and used for this use indefinitely.</p>	41 FR 56703	1976
<p>All other registration of pesticide products containing mirex canceled December 29, 1976. Existing stocks distributed, sold, and used until December 31, 1977.</p>	41 FR 56703	1976

3.2.2 *Manufacture and Distribution of Mirex*

Mirex was originally synthesized in 1946, but was not commercially introduced in the United States until the late 1950's when it was produced by the Allied Chemical Company under the name GC-1283 for use in pesticide formulations and as an industrial fire retardant under the trade name Dechlorane. Several formulations of mirex have been prepared in the past for various pesticide uses including use as baits made from corn cob grit impregnated with vegetable oil and various concentrations of mirex. Insect bait formulations contained 0.3-0.5% mirex; fire ant formulations contained 0.075-0.3% mirex.

Mirex is no longer produced commercially in the United States. Past commercial production was associated with three companies. Hooker Chemical Company, located in Niagra, NY, manufactured and processed mirex from 1957-1976. During this period, an estimated 3.3 million pounds (1.5×10^6 kg) of mirex were produced with peak production occurring between 1963 and 1968. About 25% of the mirex produced was used as a pesticide and the remaining 75% was used as an industrial fire retardant additive. The Nease Chemical Company of State College, Pennsylvania, manufactured mirex from 1966 - 1974. Allied Chemical Company also manufactured technical grade mirex and mirex bait in Aberdeen, Mississippi, through 1976 (USDHHS 1995).

3.2.3 *Mirex Use*

Mirex was marketed primarily as a flame retardant additive in the United States from 1959 to 1972 under the trade name Dechlorane for use in various coatings, plastics, rubber, paint, paper and electric goods. Over 50,000 lbs (22,700 kgs) of mirex were sold to companies in the Great Lakes watershed between 1963 through 1976. The majority was used in the Lake Erie watershed where six companies purchase almost 45,000 lbs (20,430 kgs). Over 80% of that was purchased by the Stauffer-Walker Company in Adrian, Michigan (located just southwest of Detroit) to produce a type of silicone which was used as a potting agent by RCA for television electrical components. Table 3-7 shows the amounts of mirex sold to US companies listed by Great Lakes watersheds.

Table 3-7 Amounts of Mirex sold to US companies

Watershed	Years Purchased	Total Amount Purchased (lbs)
Lake Michigan	1963-1972	1,960
Lake St. Claire	1963-1966	2,860
Lake Erie	1963-1972	44,970
Lake Ontario	1963-1964	115

In the 1960's, mirex was also used in the southern U.S. as an insecticide to control fire ants. Because of its selectiveness and effectiveness against ants, mirex was also used to control various

ant populations in the Western United States and other parts of the world, including South America and South Africa. Historical domestic use of mirex as a pesticide for fire ant control resulted in spraying of this chemical on approximately 132 million acres of soil in the southern United States. An estimated 226,000 kg of mirex was used at 9 sites between 1962 and 1976 as part of a Department of Agriculture Program (USDHHS, 1995). It was also used to control mealy bugs in pineapples in Hawaii and yellow-jacket wasps in the continental United States.

Although all pesticide uses of mirex were canceled in 1977, it appears to still be marketed as dechlorane by a company called Skylighter, Inc. for use in pyrotechnics as a chlorine donor to enhance color. However, discussion with Skylighter, Inc. revealed that the stocks being sold were old and requests for it were few. The company did not intend to purchase more Dechlorane. There is also reference to the use of Dechlorane as a chlorine donor to enhance color in "Military and Civilian Pyrotechnics" by Herbert Ellern (1968). However, this reference notes that dechlorane is not the preferred "chlorine donor" and is rarely used. No additional information was available on past or current uses of Dechlorane in the pyrotechnics industry.

3.2.4 Description of Structure/ Manufacturing Byproducts (Contaminants) and Post Manufacturing Degradation Products

Technical grade mirex (CAS # 2385-85-5) consisted of a white crystalline solid containing 95.18% mirex with 2.58 mg/kg chlordecone (also known as kepone) as a contaminant. The physical properties of mirex are given in Table 3-8. The chemical structure of mirex (Figure 3-4) makes it highly resistant to both chemical and biological degradation. The primary process for the degradation of mirex in the environment is photolysis in water or on soil surfaces, to photo-mirex.

Biological degradation in soil, both aerobic and anaerobic, are very slow and are considered minor degradation processes. Mirex has a high bioconcentration factor (BCF up to 15,000 for rainbow trout) resulting in high concentrations being found in some aquatic organisms.

Table 3-8. Physical Properties of Mirex

Properties	Value
Melting Point	485° C
Boiling Point	not available
Henry's Law Constant (KH)	not available
Log K _{oc}	not available
Log K _{ow}	not available
Water Solubility	<0.1 g/100 mL @ 24°C (1)
Vapor Pressure	3x10 ⁻⁷ mm Hg @ 25°C

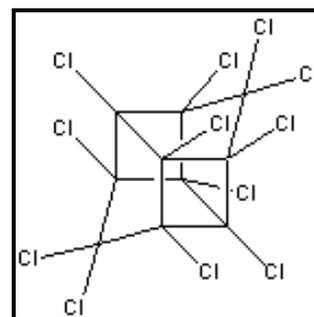


Figure 3-4. Mirex Molecular Structure

Source: Ritter *et al.*, Assessment Report, Dec 1995 (PCS 95.39) (1) Chemfinder

3.2.5 Product Import/Export

Mirex has reportedly been imported to the United States from Brazil, but data on the amounts of mirex imported are not available (USDHHS 1993). Canada estimated that approximately 50,000 pounds of mirex were sold to American companies within Great Lakes Watersheds during the period of 1963-1976, although the source of the mirex was unclear since Canada did not manufacture mirex (Fisheries and Environment Canada, 1977).

Over 90% of the mirex exported from the United States from the 1950s until 1975 was exported to Latin America, Europe, and Africa. It appears the remaining 10% was exported to Canada. Details of the amounts and locations of export of mirex to Canada were provided in a 1977 Canadian report entitled "Mirex in Canada" (Fisheries and Environment Canada, 1977) which indicated that over 300,000 pounds of mirex were imported to Canada during the period of 1963-1968. The majority of the mirex imported into Canada was under the trade name Dechlorane and was used by various industries as a flame retardant in products produced. These products were often sold back to the United States.

3.3 Chlordane

Chlordane is a man-made chemical pesticide, sometimes referred to by its trade names Octachlor® or Velsicol 1068®. Chlordane was originally used as a pesticide on field crops such as corn and citrus fruits, and later used to control termites in homes. Pesticide uses were canceled in April 1988 due to concern over human cancer risk, evidence of human exposure and accumulation in body fat, environmental persistence, and danger to nonpest wildlife.

3.3.1 Registration and Classification Status of Chlordane

United States. Regulatory actions related to chlordane use in agriculture began in 1978. All aboveground uses were stopped in the United States by 1983. Between 1983 and 1988, the sole registered use of chlordane was for subterranean control of termites. By 1988, all commercial uses of chlordane were canceled. In 1995, Velsicol, the sole US manufacturer, voluntarily canceled its export registration and by 1997 completely stopped all production in the United States and abroad and exported all existing stocks (NARAP 1997a).

There are no maximum residue levels for U.S. food commodities, although there are agency "action levels" for a variety of crops, most of which do not exceed 0.1 ppm. (the action level in fish is 0.3 ppm.) (NARAP, 1997a).

Table 3-9 summarizes the registration and classification history of chlordane in the United States.

Additional information on the regulatory status of chlordane in both Canada and Mexico is available as a result of work done by the North American Working Group for the Sound Management of Chemicals' Task Force on DDT and Chlordane in the document "North American Regional Action Plan on Chlordane" (NARAP, 1997a). This information is summarized below.

Canada. Chlordane was first registered in Canada in 1949 for the control of insect pests in crops and forests, as well as for domestic and industrial applications. It was never manufactured in Canada. (NARAP, 1997)

Most Canadian uses of chlordane were phased-out by the mid-1970s. In December 1985, with the exception of its use to control subterranean termites by licensed pesticide applicators, applications for the use of chlordane were suspended. Use against termites was voluntarily discontinued by the registrant in 1990, with the understanding that the existing stock would be sold, used or disposed-of by the end of 1995. After this date, any sale or use of chlordane in Canada represents a violation of the *Pest Control Products Act* (NARAP, 1997a).

Pesticides that are not legally registered in Canada are refused entry and returned to the exporter. The Importation for Manufacturing and Export Programme for Pest Control Products does not allow for the importation of chlordane for the purposes of reformulation and subsequent export. Any future exports of chlordane would be subject to notification according to the *Canadian Environmental Protection Act*. No such notifications have been received (NARAP, 1997a).

There are no maximum residue levels for chlordane in food commodities in Canada. An action level of 0.1 ppm is in effect for residues of chlordane in dairy products and meat and meat byproducts. This level has been established based on monitoring information collected on domestic and imported foods and is periodically revised as new information becomes available. (NARAP, 1997a)

Table 3-9. Chlordane (CAS 57-47-9) Registration and Classification History

Action	Federal Register Notice	Action Date
Notice of Intent to cancel all registered uses of chlordane and heptachlor, except for subsurface injection to control termites and dipping roots and tops of non-food plants.	39 FR 41298	11/74
41 FR 7552 suspended registrations for all pesticide products containing heptachlor or chlordane for use on corn pests, on household, garden, lawn, and turf pests (both by private homeowners and by pesticide control operators), against ticks and chiggers, and as a constituent in shelf paper. Suspension and prohibition for use on corn pests effective August 1, 1976. Stocks formulated into products intended for such uses after July 29, 1975, were not to be placed into commerce, sold, or used.	41 FR 7552	12/75
Cancellation and phase-out of registrations. Between 1978 and 1983 uses of chlordane and heptachlor were phased out; only termite control and fire ant use remained.	43 FR 12372	78-83
Voluntary termiticide registration cancellation by Velsicol Chemical Corporation. Existing stocks could be sold, distributed or used according to label until November 30, 1987. From December 1, 1987 until April 15, 1988, termiticide was for retail sale and to be used only by certified applicators or persons under their direct supervision according to the Order. No sale, distribution or use of stocks permitted after April 15, 1988.	52 FR 42145	10/87
Chlordane/Heptachlor termiticide registrations canceled. No sale, commercial use or commercial application of existing stocks allowed after April 15, 1988. Velsicol Chemical Corporation retained two "export only" registrations for chlordane. Neither of these registrations authorized sale or use in the United States.	53 FR 11798	4/15/88
Velsicol requested voluntary cancellation of their export registration for chlordane. EPA granted voluntary cancellation.	60 FR 46592	10/95

Mexico. In 1973, Mexican authorities included chlordane among registered pesticides (as a 50 percent technical ingredient) for its direct application to soils. Reference was also made to twelve other formulations in different percentages. In 1978, 31 formulations were registered and permitted for use in Mexico to control pests in corn and sorghum (with active ingredient concentrations ranging between 5 and 40 percent). In 1988, chlordane was listed as a restricted pesticide (NARAP, 1997a).

In 1989, the first Official Catalogue of Pesticides, published by the Interministerial Commission for the Control of Production and Use of Pesticides, Fertilizers and Toxic Chemicals

(Cicoplafest), states that “[chlordane] can only be applied under the supervision of trained and authorized personnel.” From 1992 until 1996 (the date of the last publication of the Cicoplafest catalogue), the only authorized use of chlordane was in "urban use" for the control of termites in installations, structures, and wood construction. Currently, “urban use” is defined as “use in residential zones, ...[a] primary use being on telephone poles.” Product labels must include the statement that the chemical can be applied only by authorized personnel in urban areas (NARAP, 1997a).

In 1997, there remained nine registered uses of chlordane in Mexico: one for technical grade chlordane and eight for the formulated product in concentrations ranging between 380 and 500 g/l (NARAP, 1997a). However, according to the NARAP on Chlordane, the goal is to phase-out existing registered uses of chlordane in Mexico by identifying alternative effective termite control strategies in Mexico.

3.3.2 Manufacture and Distribution of Chlordane

The sole U.S. manufacturer of chlordane was Velsicol Chemical Corporation in Memphis, Tennessee. On the basis of historic production figures, an estimated 70,000 tons of chlordane were produced since 1946, of which 25-50% is reported to still exist unaltered in the environment (Dearth and Hites 1991b). NSC (1997) reports EPA data that between 3.5 and 4 million pounds of chlordane were distributed in 1986. In May 1997, Velsicol announced that it had voluntarily ceased production of chlordane in the United States and around the world. (NARAP, 1997a)

3.3.3 Chlordane Use

Chlordane’s primary use in the United States was as a pesticide from 1948 to 1988. In 1978, EPA canceled the use of chlordane on food crops and phased out all other above-ground uses during the following five years. EPA Office of Groundwater estimates that before 1983 “greater than 3.6 million pounds” of the chlordane pesticide was used annually in the United States. All aboveground uses were stopped in the United States by 1983. Between 1983 and 1988, chlordane was only approved for subterranean control of termites, primarily poured or injected around building foundations.. The last approved application (*i.e.*, for termites) was canceled in April 1988.

Multiple sources (e.g.,USDHHS, 1994; NSC, 1997) report that in the mid 1970's, 35% of the commercial product was used by pest control operators (mostly on termites), 28% on agricultural crops (including corn, citrus, deciduous fruits, nuts, and vegetables); 30% for home lawn and garden use; and 7% on turf and ornamentals. Commercial products were usually applied directly to soil or foliage to control a variety of insect pests including parasitic roundworms and other nematodes, termites, cutworms, chiggers, leafhoppers.

NSC (1997) reports National Wildlife Foundation information that, in 1987, before the final use of chlordane was canceled, 2,614 pounds of the pesticide were released into the air [Illinois (884

lbs), Mississippi (500 pounds), and Tennessee (1,230 pounds)]. Documented releases of chlordane to the environment from US production and handling facilities, according to the 1990 TRI, indicated that a total of 4,423 pounds were released to the air. EPA's 1996 TRI, the most recent year available, reports 660 pounds (300 kg) of chlordane as fugitive or non-point air emissions and 95 pounds (43 kg) as surface-water discharges.

3.3.4 Description of Structure/Manufacturing Byproducts (Contaminants) and Post-Manufacture Degradation Products

Pure chlordane's chemical formula is $C_{10}H_6Cl_8$. Its molecular weight is 409.76. The physical properties of chlordane are given in Table 3-10. Technical chlordane (CAS No. 57-74-9) is a mixture of greater than 140 related compounds. These commercial products are thick viscous liquids, whose color range from colorless to amber, depending on purity. 60-85% of technical chlordane mixtures consist of the stereo-isomers cis- (α -chlordane) and trans- (γ -chlordane) chlordane (CAS No.'s 5103-71-9 and 5103-74-2, respectively). Figure 3-5 shows the molecular structure of *trans*-chlordane. Because of the many compounds that comprise the technical mixture, the physical and chemical properties of chlordane are difficult to specify. Many of the compounds are solids when pure, but form a viscous liquid when mixed (eutectic mixture). The vapor pressures of the pure components of chlordane are lower than the technical product because the solids have crystal lattice energies that reduce their vapor pressures. Furthermore, the vapor pressure of the mixture changes as the more volatile compounds vaporize. For these reasons, the physical properties of many constituents of technical chlordane are unknown or uncertain, and, correspondingly, there is uncertainty regarding degradation and transport of specific compounds (USDHHS, 1994).

If burned, chlordane emits a poisonous gas. Chlordane is very persistent in the environment. It is resistant to both chemical and biological degradation and is strongly bioaccumulated in fish and other aquatic organisms.

Table 3-10 Physical Properties of Technical Chlordane

Properties	Value
Melting Point	<25° C - technical 106° C - cis-chlordane 104° C - trans-chlordane
Boiling Point	165-175° C @ 2 mm Hg
Henry's Law Constant (KH)	4.8x10 ⁻⁵ atm m ³ /mol @25° C 8.31x10 ⁻⁵ atm m ³ /mol @25° C (trans-)
Log K _{oc}	4.58-5.57
Log K _{ow}	5.54 - 6.00
Water Solubility	56 ug/L at 25° C (cis:trans 75:25)
Vapor Pressure	10 ⁻⁶ mm Hg @ 20° C

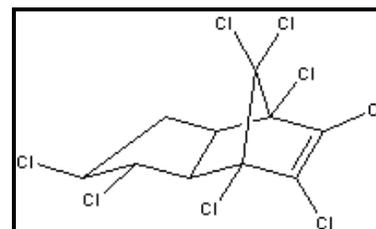


Figure 3-5. Chlordane Molecular Structure

Source: Ritter *et al.*, Assessment Report, Dec 1995 (PCS 95.39); USDHHS, 1994

If released to soil, chlordane persists for long periods. Under field conditions, the observed mean degradation rate ranges from 4.05-28.33%/yr with a mean half-life of 3.3 years. If released to water, chlordane does not significantly undergo hydrolysis, oxidation, or direct photolysis. Chlordane degrades in air by both photolysis and oxidation. Chlordane will react in the vapor-phase with photochemically produced hydroxyl radicals at an estimated half-life of 1.3 - 6.2 hr (USDHHS, 1994).

3.3.5 Product Imports and Exports

No chlordane was imported to the United States. The only U.S. manufacturer, Velsicol Chemical Company, requested voluntary cancellation of their export registration. EPA granted the cancellation in October 1995 (60 FR 46592).

The only export data found for this report was 1990 to 1996 data in the North American Regional Action Plan on Chlordane (NARAP, 1997a). In recent years, there has been no chlordane manufacturers in Mexico. In Mexico, Velsimex prepares formulations of chlordane pesticides from imported ingredients. During 1990-1996, Velsimex imported 212.8 tonnes of technical product to Mexico from the United States. The 1992-1996 import quantities are shown in Table3-11.

Table 3-11. Mexican Chlordane Imports from United States

Year	Quantity (metric tons)
1992	74.4
1993	37.2
1994	82.6
1995	0
1996	18.6

3.4 DDT

DDT [1,1,1-trichloro-2, 2-bis-(*p*-chlorophenyl)ethane] is a broad spectrum insecticide, used on crops, grazing land, forest and urban areas to control insects that transmit diseases such as malaria and typhus. DDT does not occur naturally. Its presence in the environment is the result of contamination from past production, use, disposal, and transport by air and water.

3.4.1 Registration and Classification Status of DDT

After studying the persistence of DDT residues in the environment, the U.S. Department of Agriculture (USDA) canceled the registration of certain uses of DDT (on shade trees, on tobacco, in the home, and in aquatic environments) in 1969. Applications on crops, commercial plants, wood products, and for building purposes were canceled by the USDA in 1970. Under the authority of the EPA, the registrations of the remaining DDT products and DDT-metabolites were canceled on 4 January 1973, with the following exemptions:

- Public-health use for control of vector-borne diseases,
- USDA or military use for health quarantine, and
- Use in prescription drugs for controlling body lice.

By October 1989, the remaining three uses were voluntarily canceled due to failure to pay maintenance fees. The fact that there is no U.S. registration for DDT means that the compound cannot be used in the United States.

DDT is not currently manufactured in the United States. However, as with other pesticides, the United States does not have the legislative authority to prohibit production of DDT if a manufacturer wanted to initiate such production in the future.

Table 3-12 summarizes the U.S. registration and classification history of DDT.

Table 3-12. DDT (CAS #50-29-3) Registration and Classification History

Action	Federal Register Notice	Action Date
Registrations canceled for following uses: Foliar pre-plant soil application, and bait uses on alfalfa (except when grown for seed only), barley, clover (except when grown for seed only), birdsfoot, trefoil, grasses, lespedeza (except when grown for seed only), millet, milo, pasture grass, rice, rye, sorghum, vetch (except when grown for seed only), and forage legumes.	34 FR 7712	5/69
Registrations canceled for the following uses: Alfalfa (seed crop), bananas, barley, buckwheat, clover (seed crop), corn (field and pop), corn (seed), dates, figs, flax, horseradish, Jerusalem artichokes, lespedeza (seed crop), milo, oats, olives, parsley, passion fruit, persimmons, pomegranate, rice, rye, safflower, salify, sorghum, sugar beets, sugarcane, sweet potatoes (pre-harvest), vetch (seed crop), and wheat.	35 FR 7135	5/70
All uses of DDT for crop production and nonhealth purposes canceled.	37 FR 13369	12/72
Exemption granted for use on the Douglas-Fir Tussock Moth.	39 FR 8377	1974
Limited use registration for dry peas approved to control the pea leaf weevil in Washington and Idaho.	39 FR 10322	73/74
Registration approved for control of head and body crab louse and scabies.	40 FR 2612	1975
Louisiana's request for emergency use of DDT on cotton denied.	40 FR 15934	1975
Massachusetts Department of Public Health granted crisis exemption to use DDT to control rabid bats.	40 FR 43758	1975
New Jersey Department of Environmental Protection granted crisis exemption to use DDT to control rabid bats.	40 FR 43759	1975
New Hampshire Division of Public Health Services granted crisis exemption to use DDT to control rabid bats.	41 FR 816	1976
Pennsylvania granted crisis exemption to use DDT to control rabid bats.	41 FR 6122	1976
Delaware Department of Agriculture granted crisis exemption to use DDT to control rabid bats.	41 FR 7809	1976
California Department of Health granted exemption for use of DDT to control flea vectors of plague	41 FR 22979	1976

Table 3-12. DDT (CAS #50-29-3) Registration and Classification History

Action	Federal Register Notice	Action Date
Experimental use permit issued to Clemson University to evaluate effectiveness in controlling the cotton bollworm and the tobacco budworm.	41 FR 35096	1976
Exemption granted to the State of Colorado for use of DDT dust to suppress flea populations.	41 FR 36250	1976
Registration granted to CDC for DDT 50% wettable powder, intended for use in rabies vector control programs.	41 FR 31253	1976
DDT and TDE food and feed additive regulations revoked.	51 FR 46616	12/86
DDT and TDE tolerances revoked.	51 FR 46658	12/86

Canada. In Canada, most uses of DDT were phased out in the mid-1970s, and registration for remaining uses was discontinued in 1985. Canada allowed use of existing stocks through December 1990.

Mexico. DDT is still currently being used in Mexico, though application is restricted to malaria control programs.

3.4.2 Manufacture and Distribution of DDT

DDT is made by condensing chloral hydrate with chlorobenzene in the presence of sulfuric acid. It was first synthesized in 1874; insecticidal properties were discovered in 1939. The pesticide was marketed as aerosols, dustable powders, emulsifiable concentrates, granules, and wettable powders. It is reported to be compatible with many other pesticides and incompatible with alkaline substances (EXTOXNET 98).

U.S. DDT production peaked in 1962 at 82 million kg. Production declined to 56 million in 1968, and to 2 million kg/yr in 1971. Currently, no U.S. companies manufacture DDT (as reported in USDHHS, 1993). However, there are current manufacturers in India, China and Mexico. There is only one manufacturer in Mexico that supplies the country's malaria-control human-health programs only and production is subject to Government approval (refer to Section 3.4.5).

3.4.3 Product Use

United States. DDT's only known use in the United States was as a contact pesticide. It was applied to crops and forests, and sprayed directly on animals (mostly cattle) and human beings. Major uses were to control cotton crop pests and mosquitoes. U.S. agricultural use occurred from about 1945 to 1972. Figure 3-6 shows the use in pounds of DDT by state in 1970 (Majewski and Capel, 1995) as well as the concentrations found in air measured in from

1960-1970 and the detection frequency relative to the number of sites sampled for air measurements. DDT application appeared highest in the Southeastern U.S. *p,p'*-DDT was detected in almost all of the air samples collected (similar statistics showed slightly lower detection frequency of *o,p'*-DDT), however, it is important to remember that these samples were collected in the 1970s during and shortly after actual application of the pesticide. More recent atmospheric measurements show a trend toward lower DDT detection and higher detection of the primary breakdown product, DDE.

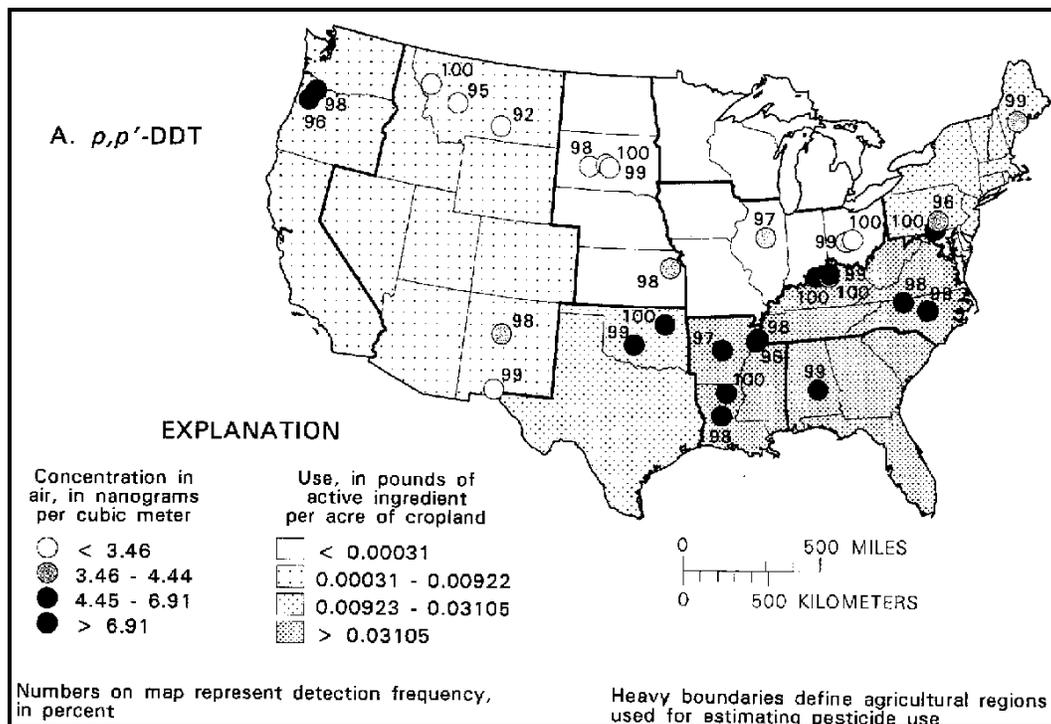


Figure 3-6. Average range of measured concentrations *p,p'* in air and the detection frequency at each sampling.

NOTE: Concentrations measured from 1960-1970; agricultural use in 1970.

Source: Pesticides in the Atmosphere, Distribution, Trials & Governing Factors (Majewski & Capel, 1995)

The last public health use was in the late 1970s. Product manufacture and use continues outside the United States. Most relevant to the Great Lakes program is DDT manufacture and application for Mexico's malaria control program. DDD was also reported to be used as a pesticide, and one form of DDD was used medically in the treatment of cancer of the adrenal gland (USDHHS, 1993). However, no U.S. registration for DDD pesticide use was found so this may have applied to use outside of the United States.

Ninety percent of the domestically applied product was on cotton. The remaining 10% was used on vegetable, field crops, livestock, and public health campaigns to control mosquito-borne and lice-borne diseases (Spectrum, 1998). Since its initial use in the 1940s through the mid 1970s, millions of pounds of DDT were applied throughout the United States and neighboring countries.

DDT was extensively used during the Second World War among Allied troops and certain civilian populations to control insect typhus and malaria vectors; after 1945, it was primarily used as an agricultural insecticide. Ninety percent of U.S. production of DDT insecticide was exported for use outside the country (Spectrum, 1998).

In the late 1960s, the deleterious effects of DDT on the environment became well known. Sweden banned its use in 1970, and the United States canceled DDT registration for crop production and nonhealth purposes in 1972. Between 1972 and 1976, U.S. agencies granted occasional exceptions for research purposes and public health crises. Under the Emergency Planning and Community Right-to-Know Act of 1986, releases of more than one pound of DDT, DDE and DDD into the air, water, or land must be reported annually and entered into the national Toxic Release Inventory (TRI) data base. A query of TRI database in September 1998 reveals no reported air, water, or land releases of DDT from U.S. facilities between 1987 and 1996.

Mexico. Similar to its pattern of use in the United States and Canada, DDT's introduction in Mexico in the early 1950s was for use in agriculture. In the 1970s, DDT use in agriculture production declined due to environmental concerns and introduction of stricter limits by the USDA on residues of DDT on imported foods.

Agricultural use of DDT in northern Mexico started to decline in the 1970s when the U.S. Department of Agriculture (USDA) began rejecting Mexican produce imports containing high residue levels of DDT. In southern Mexico, where fewer crops are exported to the United States, use of DDT on crops declined at a slower rate. In 1990, Mexico banned DDT and five other persistent organochlorine pesticides from agricultural use.

Today, DDT is registered in Mexico only for use in government-sponsored public health campaigns to control malaria where it is still considered an important tool in the fight against malaria transmission. In the 1940s and 1950s, malaria was one of the main causes of mortality in Mexico, responsible for an average of 24,000 deaths annually and afflicting an estimated 2.4 million others. In recent years, the incidences of malaria have declined significantly to less than 5,000 cases. Since 1982 there have been no deaths from malaria. This success has occurred while alternative methods of pest control have been employed, resulting in a significant decline in DDT use.

There is only one private company producing DDT in Mexico, and its production is subject to government approval. Mexican production of DDT is presently less than 600 tonnes per year (NARAP 1997).

Other countries where DDT has been prohibited include Argentina, Australia, Bulgaria, Colombia, Cyprus, Ethiopia, Finland, Hong Kong, Japan, Lebanon, Mozambique, Norway, and Switzerland. Countries such as Mexico that severely restrict DDT use include Belize, Ecuador, the EU, India, Israel, Kenya, Panama, and Thailand.

3.4.4 Product Components/Structure, Manufacturing Byproducts (Contaminants) and Post-Manufacture Degradation Products

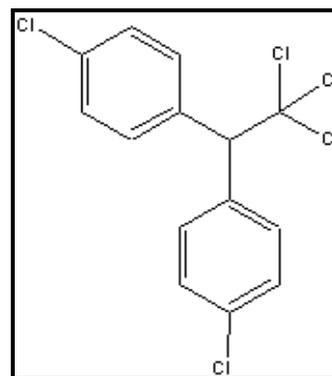
The chemical formula for DDT (CAS 50-29-3) is $C_{14}H_9Cl_5$. The physical properties of DDT are given in Table 3-13. Figure 3-7 shows the molecular structure of DDT. DDT is highly insoluble in water and is soluble in most organic solvents. It is semi-volatile and can be expected to partition into the atmosphere as a result. Technical DDT is primarily composed of three forms: p,p'-DDT (85%), o,p'-DDT (15%), and o,o'-DDT (trace), all of which are white, crystalline, tasteless, and almost odorless solids. DDE [1,1-dichloro-2, 2-bis(p-chlorophenyl)ethylene] and DDD [1,1-dichloro-2, 2-bis(p-chlorophenyl)ethane] are found in small amounts as contaminants in technical DDT.

DDT is also an intermediate/reactant for dicofol, a miticide registered for use in the US, Canada and Europe. The U.S. imports dicofol which must contain less than 0.1% DDT (USEPA, OPPT registration standard). USGS Pesticide Monitoring Program estimated that approximately 1.1 million pounds of dicofol is applied in the United States annually. Based on this estimate, it would appear that about 1000 pounds of DDT are being applied to croplands in the United States annually. Figure 3-8 illustrates the use patterns and lists the percentage used on each crop.

Table 3-13. Physical Properties of DDT

Properties	Value
Melting Point	108°C -109°C p,p' 74°C - 75°C o,p'
Boiling Point	260° C@ 2 mm Hg
Henry's Law Constant (KH)	5.13x10 ⁻⁴ atm m ³ /mol @25°C
Log K _{oc}	5.38
Log K _{ow}	6.19
Water Solubility	3.4 ug/L at 25°C
Vapor Pressure	5.5x10 ⁻⁶ torr @ 20°C

Source: USDHHS, 1992



**Figure 3-7. DDT
Molecular structure**

In general, DDT is very persistent in the environment and resistant to degradation. The major degradation product of DDT is DDE. (USDHHS 1992).

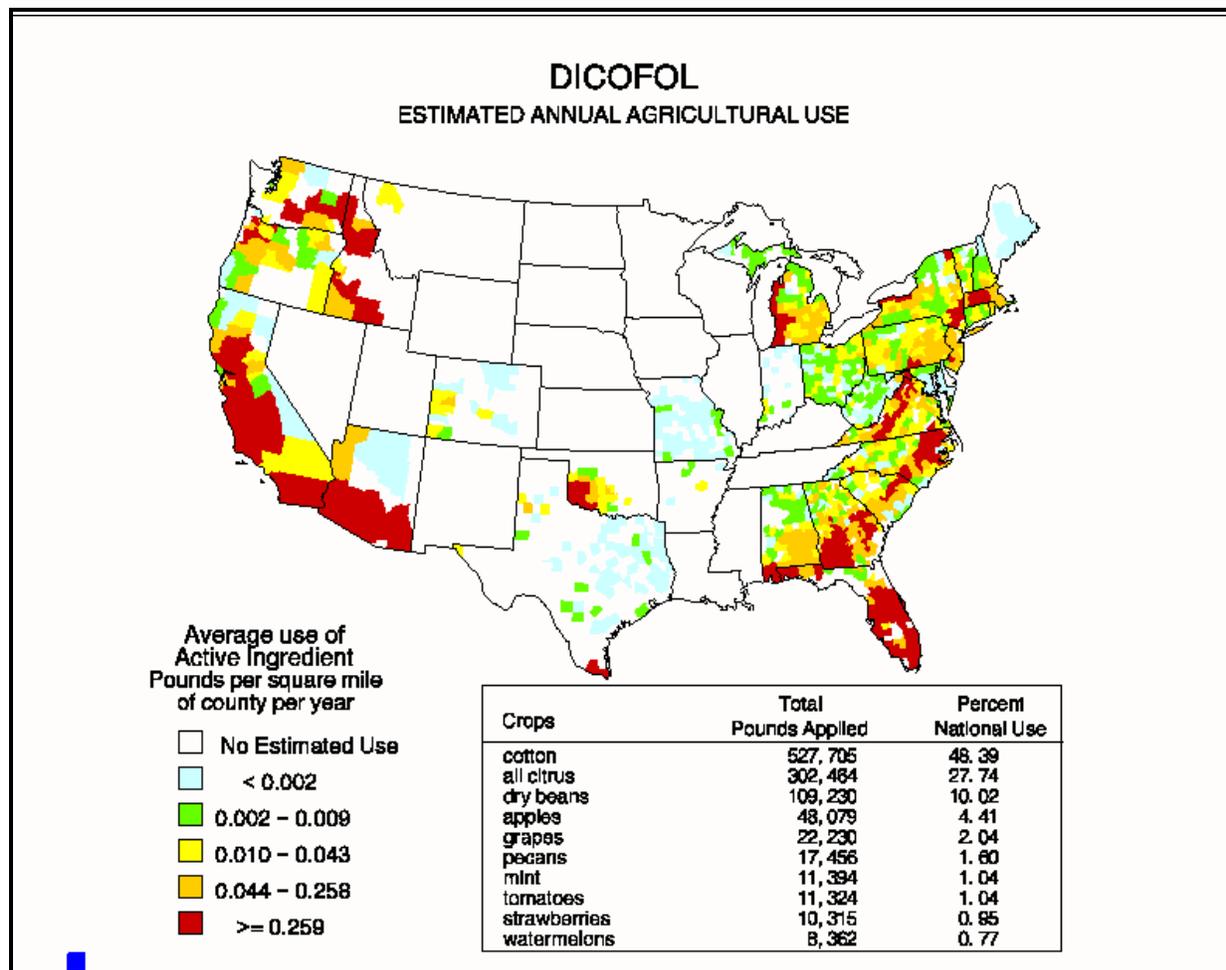


Figure 3-8. DICOFOLE estimated agricultural use and annual application quantities

Source: <http://water.wr.usgs.gov/pnsp/use92/dicofol.html>

3.4.5 Product Imports and Exports

There are no reports of DDT pesticide currently being imported or exported for commercial purposes in the United States, and no known current U.S.-based manufacturers. The most recent export data found for this study was 303,000 kg exported in 1985 (NSC Envir. Writer, 1997).

Recent reports of DDT exports leaving the United States have been attributed to shipment of small research quantities (e.g., reference standards shipped between laboratories) that are subject to the export-notification requirements of the Toxic Substances Control Act (TSCA), which has no *de minimis* cutoff for notification. Similarly, imports of DDT to the United States have occurred when the Department of Defense (DOD) recalled its existing stocks for destruction. The U.S. DOD no longer uses DDT in any of its operations abroad and does not maintain a stockpile (NARAP, 1997b).

3.5 Toxaphene

Toxaphene is a chlorinated insecticide known as camphechlor and Strobane-T, among other names (See Table 3-1). In its pure form, toxaphene is a yellow waxy solid with an odor similar to turpentine. Like chlordane, toxaphene is not a single compound, but rather a complex mixture of many different chemicals. The use of toxaphene as a pesticide was canceled in the United States in 1990 because of evidence of human and animal health risks.

3.5.1 Registration and Classification Status of Toxaphene

In 1982, EPA restricted toxaphene use to control livestock ecto parasites, and to control grasshoppers and army worm infestations on cotton, corn, small grains (in emergency situations) in the continental United States, and on bananas and pineapple crops in Puerto Rico and the Virgin Islands (Table 3-14). The remaining U.S. registered uses of toxaphene were canceled in 1990. EPA additionally prohibited the importation of food containing toxaphene residues in 1993, when the food tolerances from DDT residues were revoked.

3.5.2 Manufacture and Distribution of Toxaphene

Toxaphene is a manufactured insecticide, first produced in 1946. In 1972, toxaphene was the most heavily manufactured pesticide in the United States. Its use became prevalent because of the demand for replacement compounds for DDT. The major manufacturers during peak production were limited to three U.S. companies (Hercules Inc., Tenneco and Vicksburg Chemical Co.). The name "Toxaphene" was the trademark of the Hercules company. Slightly different manufacturing processes used by other companies resulted in chlorinated camphene mixtures with degrees of chlorination and congener distributions that are not the same as the Hercules Incorporated product. However, over the years, the name toxaphene has come to refer to all of these mixtures. Toxaphene is no longer produced in the United States.

3.5.3 Toxaphene Use

Prior to 1982, toxaphene was one of the most heavily used insecticides in the southern United States. Toxaphene was used agriculturally in the United States to control insects living on cotton, peas, corn, fruit, vegetables, and small grains such as rice, in addition to other crops. It acts as a nonsystemic stomach and contact insecticide. Toxaphene has a relatively low toxicity to bees, and therefore was used to treat many flowering plants. In addition to its use as a crop insecticide, toxaphene was also used to control livestock parasites such as scabies, lice, flies, ticks, and mange.

Toxaphene was also used, often in combination with rotenone, to eradicate fish considered undesirable for sport fishing. This practice was most commonly performed in Canada and the northern U.S. This use of toxaphene actually aided in the identification of its persistence in the environment due to the difficulty in establishing desirable fish species into lakes/water bodies previously treated with the pesticide. Results of a study of Wisconsin lakes treated with 100 ppb

toxaphene indicated that the lakes could not be safely re-stocked with game fish for approximately five years.

In 1974, an estimated 20 million kg of toxaphene were used in the U.S., primarily on cotton crops. Between 1975 and 1982, manufacturing production levels decreased dramatically, from 27 million kg in 1975, to less than 2 million kg in 1982. In 1982, EPA canceled the registration of toxaphene for most pesticidal uses and all remaining uses were canceled in 1990.

Toxaphene is banned in seven countries and the EEC, and is severely restricted in eleven countries. Toxaphene and toxaphene-like pesticides currently do not appear to be produced in any other countries. Data indicate that toxaphene was most recently produced in 1992 in Mexico, India and Russia (Ritter et al., 1995). It is estimated that total world-wide toxaphene use between 1950 and 1993 was greater than 1.2 billion kg. (USDHHS, 1994b)

Table 3-14. Toxaphene (CAS 8001-35-2) Registration and Classification History

Action	Federal Register Notice	Action Date
Most uses canceled except dipping of beef cattle and sheep to control scabies, use on cotton, corn or small grains to control armyworms, cutworms or grasshoppers. Continued registration permitted for use on pineapples to control mealybug and pineapple gummosis moth and use on bananas for weevil control in the Virgin Islands and Puerto Rico only. Existing stocks which consisted of or could be made into formulations suitable to control sicklepod in soybeans and peanuts in certain states with registrations, for use to control insects in corn cultivated without tillage and in dry and southern peas could be distributed, sold, offered for sale, held for sale, shipped, delivered for shipment, or received and delivered or offered for delivery until December 31, 1986. Existing stock which could not be made suitable for above uses was distributed, sold, offered for sale, held for sale, shipped, delivered for shipment, or received to be held for delivery until December 31, 1983.	47 FR 53784	10/82
Registration of toxaphene mixtures canceled. Registrants allowed to sell and distribute existing stocks for 1 year after cancellation. Dealers and users allowed to sell or use stock until exhausted.	55 FR 31164	7/90
Tolerances and food additive regulations revoked.	58 FR 46087	9/93

3.5.4 Structure/Manufacturing Byproducts (Contaminants) and Post-Manufacture Degradation Products

Toxaphene (CAS 8001-35-2) is a multi-component mixture, and cannot be adequately represented by a single chemical formula or structure. Its physical properties are given in Table 3-15. It is a reproducible mixture of at least 177 C₁₀ polychloro derivatives produced by chlorinating camphene to 67 to 69% chlorine. It's overall empirical molecular formula can be summarized as C₁₀H₁₀Cl₈. It does not readily burn, and evaporates when in solid form or when mixed in a liquid. Toxaphene is only slightly water soluble, and therefore usually associated with particulates - suspended solids or sediment/soil, or on particulates in air.

Toxaphene has a half-life in water of >200 days, and has an estimated half-life of 1 to 14 years in soil, classifying it as relatively persistent.

While byproducts of toxaphene itself are not reported, polychlorinated camphenes may be accidental byproducts of chemical processes that require chlorination, such as the pulp and paper manufacturing industry (USDHHS 1994b). Research into this process as a source of toxaphene to the environment has been conducted, and studies in Sweden and Finland have detected polychlorinated terphenes near pulp mill effluents (USDHHS 1994b).

Table 3-15. Physical Properties of Toxaphene

Properties	Value
Melting Point	65°C - 90°C
Boiling Point	Not applicable (dechlorinates at 155°C)
Henry's Law Constant (KH)	0.005-0.21 atm m ³ /mol @25°C
Log K _{oc}	2.5-5.0
Log K _{ow}	3.3
Water Solubility	3 ug/L at 25°C
Vapor Pressure	5x10 ⁻⁶ mm Hg @ 20°C

Source: USDHHS, 1994b

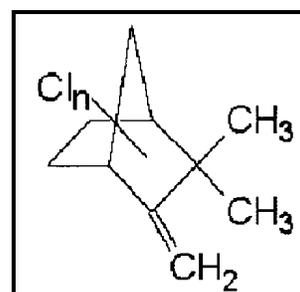


Figure 3-9. Toxaphene Molecular Structure

3.5.5 Past and Present Product Imports and Exports

No current information on toxaphene imports was found.

In 1972, approximately 35% of the total annual production of toxaphene (7.25 million kg) was exported. No other quantitative export information was found to be available (USDHHS, 1994).

3.6 Overview of Current Global Use and Production of the Level I Pesticides

Global production and use information is currently being investigated. Information provided in this table was based on non-corroborated information collected in 1997 and may not be accurate for 1999. This table will be updated in the final draft of this report.

Table 3-16 Summary of Global Production and Use

Level I Pesticide	Global Production Locations	Locations of Use
aldrin/dieldrin	India	
chlordane	India	
DDT	China, India, Argentina	
Mirex	Argentina	
Toxaphene	None	